

Analysis of Pressure-Broadened Ozone Spectra
in the 3- μ m Region

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The presence of a layer of photochemically produced ozone in the stratosphere has long been recognized as vital to life on earth, as it provides a shield from the harmful ultraviolet component of sunlight. A deficit in the ozone layer was observed over Antarctica in the mid 1980's, motivating considerable effort to improve and standardize methods of measuring and monitoring ozone in the atmosphere. More recently, increased atmospheric ozone at the earth's surface has been found to be of significant environmental concern. Spectroscopic methods are the basis for remote sensing techniques to measure atmospheric content of many chemical species, including ozone, on both global and regional scales. As technology continues to improve, the understanding of the spectra of these species becomes increasingly important in accurate retrieval of atmospheric composition data obtained by remote sensing techniques.

The Molecular Spectroscopy Lab at NASA-Langley has been involved in a long term effort to carefully and fully characterize the infrared spectra of small molecules of atmospheric interest, including methane, water vapor, carbon dioxide, and ozone, and their isotopic counterparts. High resolution gas phase infrared spectra are obtained using both a tunable diode laser system, and the McMath Fourier transform spectrometer at the Kitt Peak Solar Observatory. Spectra are obtained at various sample pressures and temperatures, both for pure gas samples, and for samples containing mixtures of the species of interest diluted in nitrogen, oxygen, or air. Air-diluted samples simulate the atmosphere at different altitudes, by varying temperature and pressure. Nitrogen- and oxygen-diluted samples allow theoretical studies of the interactions of ozone with these air components individually. Spectral parameters are modeled to the observed spectra by a non-linear least squares fitting technique. Position, intensity and half-width are determined for each well-isolated feature of reasonable intensity in the spectra. These parameters are of interest in theoretical studies, as well as in allowing more accurate interpretation of remote sensing data.

This work involves the analysis of a series of McMath FTIR spectra of ozone broadened by mixing with air (four different pressures), nitrogen (three pressures), or oxygen (three pressures). Each spectrum covers the region from 2396 to 4057 cm^{-1} . This study has focused on the $3\nu_3$ band in the 3000 to 3060 cm^{-1}

region. The band is analysed by first dividing its region into small (0.5 to 2.0 cm^{-1}) intervals containing a few well isolated absorption lines of reasonable intensity. Each of these small intervals is "fit" by multiple iterations of the non-linear least squares program until residuals (difference between calculated and observed spectrum, as a percent of the strongest intensity in the interval) are minimized to a "reasonable" value which corresponds to the noise level of the measured spectrum. Position, intensity and half-width are recorded for later analysis.

From the measured half-widths, a pressure broadening coefficient has been determined for each absorption line. These broadening coefficients are shown in Figure 1 as a function of lower state rotational quantum number. The broadening coefficients show a slight decrease with increasing rotational quantum number. Pressure shifts have been determined by comparing observed line positions in the spectra of the diluted ozone samples to tabulated line positions determined from spectra of pure gas samples. Pressure shifts are shown as a function of quantum number in Figure 2, and show little dependence on rotational quantum number. Broadening and shift coefficients for this absorption band have not been examined before, but comparisons can be made to similar studies of other ozone bands. In particular, it is noteworthy that the observed shifts for the $3\nu_3$ band are on the order of three times the shifts for the ν_1 band (1), showing a dependence on the energy of the vibration, as ν_1 occurs at about 1100 cm^{-1} and $3\nu_3$ at about 3000 cm^{-1} . It is also of interest that the broadening coefficient for air is between those of nitrogen and oxygen. In particular, the broadening coefficient for air can be expressed as a weighted average of those for nitrogen and oxygen, where the weighting coefficients are those of the relative abundance of each gas in air. Comparisons to other work on ozone (2,3,4,5) indicate that the broadening and shift coefficients determined in this study are consistent with those determined in other spectral regions.

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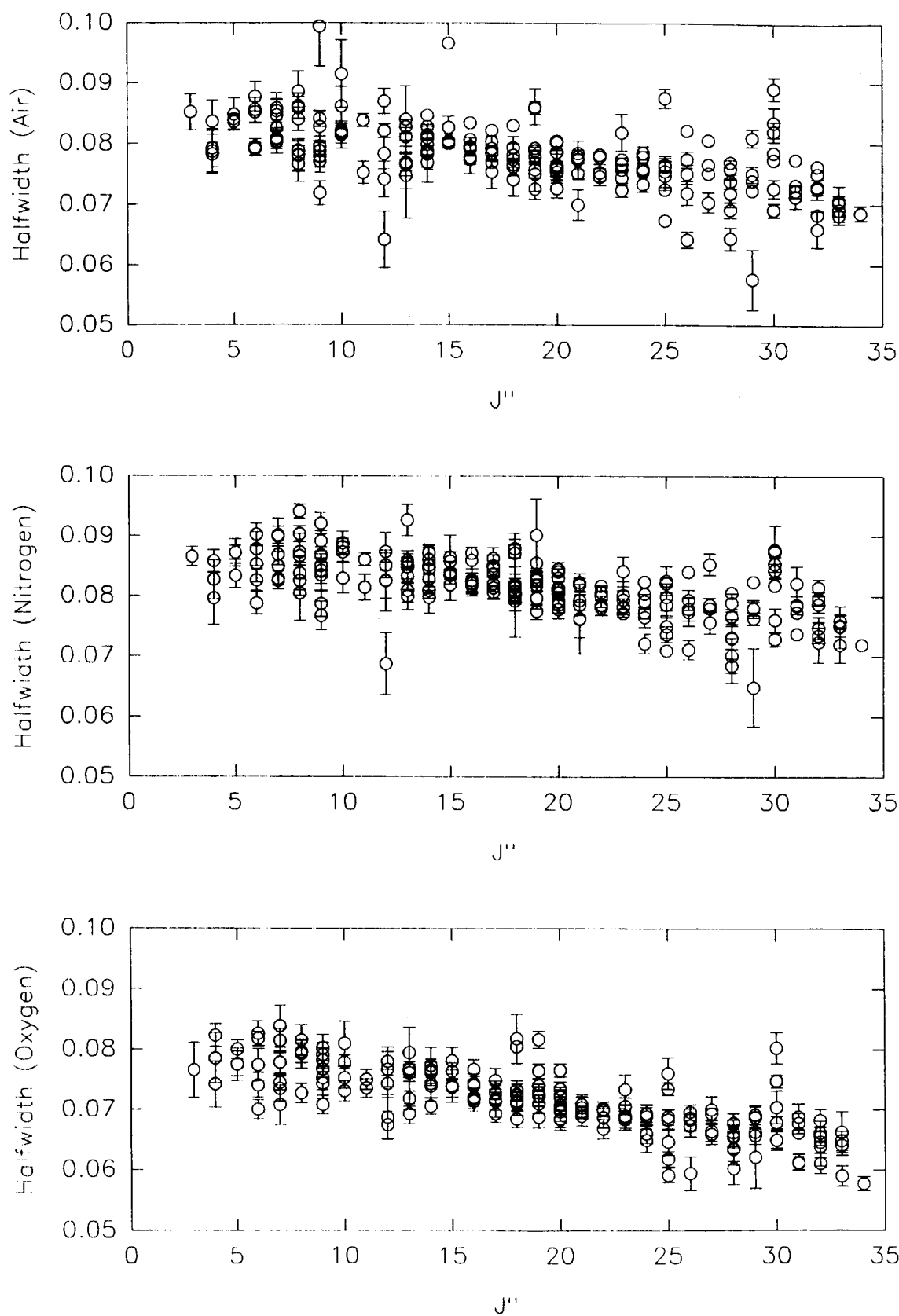


Figure 1. Broadening Coefficient ($\text{cm}^{-1}\text{atm}^{-1}$) vs Rotational Quantum Number

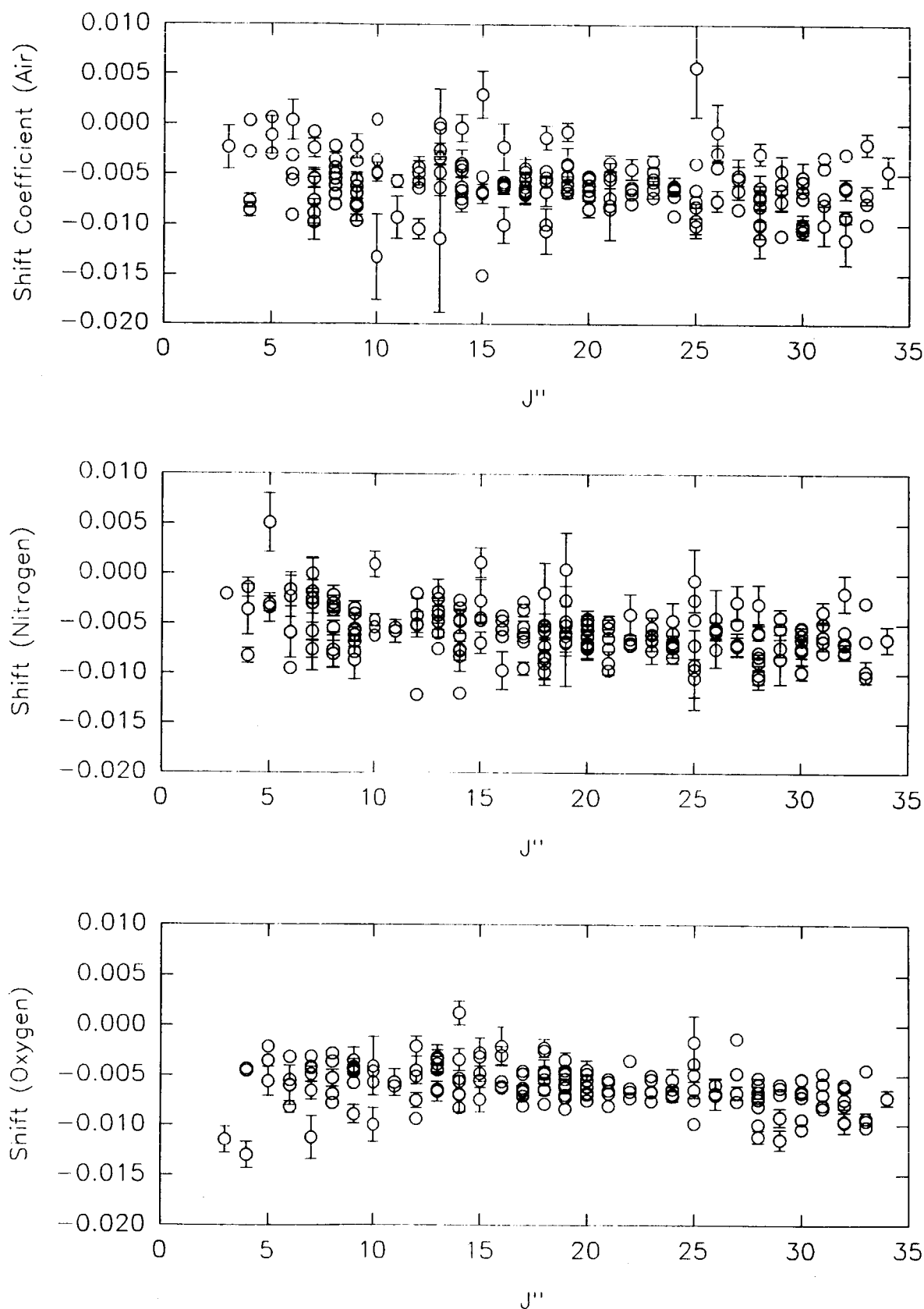


Figure 2. Shift Coefficients ($\text{cm}^{-1} \text{atm}^{-1}$) vs Rotational Quantum Number